PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C01B 17/20, 19/00, 19/04, C01G 9/02, 9/08 — A1

(11) International Publication Number: WO 98/19963

(43) International Publication Date: 14 May 1998 (14.05.98)

(21) International Application Number: PCT/US97/22420

(22) International Filing Date: 7 November 1997 (07.11.97)

(30) Priority Data:
60/029,422 8 November 1996 (08.11.96) US
08/910,160 12 August 1997 (12.08.97) US

(71) Applicant: SPECTRA SCIENCE CORPORATION [US/US]; 155 South Main Street, Providence, RI 02903 (US).

(72) Inventors: LAWANDY, Nabil, M.; 169 Eastwick Avenue, North Kingstown, RI 02852 (US). ZEPP, Charles, M.; 940 North Road, Hardwick, MA 01037 (US). ROSSI, Richard, F.; 272 Reservoir Street, Norton, MA 02766 (US).

(74) Agent: GREEN, Clarence, A.; Perman & Green, LLP, 425 Post Road, Fairfield, CT 06430 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: SYNTHESIS OF METAL CHALCOGENIDE QUANTUM DOTS FROM AQUEOUS MEDIA

(57) Abstract

An aqueous system for the production of metal chalcogenide nanocrystalline salts such as zinc selenide, from a hydrolyzable chalcogen carboxyl compound, such as selenourea, by simple hydrolysis thereof under alkaline conditions in the presence of water soluble metal hydroxide, such as zinc hydroxide in the form of the zincate ion, i.e., $Zn(OH)_4^{-2}$. Selenourea contains selenium in the correct oxidation state, is inexpensive, commercially-available and readily hydrolyzable under aqueous basic conditions in the presence of the zincate ion to form zinc selenide. The zinc selenide is insoluble in the alkaline aqueous vehicle and precipitates over time in the form of nanocrystallites or quantum dots of the zinc selenide.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

SYNTHESIS OF METAL CHALCOGENIDE QUANTUM DOTS FROM AQUEOUS MEDIA

The present application is related to co-pending Provisional patent application Serial No. 60/029,422 of Nabil M. Lawandy et al., filed 11/08/96 titled "Synthesis of Metal Chalcogenide Quantum Dots from Aqueous Media", based on which priority is herewith claimed under 35 USC 119(e) and the disclosure of which is incorporated herein by reference in its entirety.

Background Of The Invention

Field of the Invention:

The present invention relates to nanometer-sized crystallites or quantum dots having semiconductor properties, and more particularly to an improved process for synthesizing such crystallites from readily available, inexpensive starting materials and under mild reaction conditions.

State of the Art:

The synthesis of metal chalcogenide quantum dots, such as of zinc selenide, is known but the existing methods are unsatisfactory and not

amenable to scale-up. For example, Murray et al disclose a method for the synthesis of cadmium selenide quantum dots in the Journal of the American Chemical Society, Vol. 115, pages 8706-8715 (1993). This method makes use of tri-n-octylphosphine as a coordinating solvent, either elemental selenium or bis(trimethylsilyl)selenium as the chalcogenide donor, and dimethylcadmium as the metal donor. The disadvantage to this method is the nature of the reactants, most of which need to be synthesized, and the use of an expensive, air sensitive, unstable, solvent as well as the need for high reaction temperatures. This method is considered to be unsatisfactory for the production zinc selenide.

There exists a need for a process for producing metal chalcogenide nanocrystals or quantum dots from readily available, stable reactants and mild reaction conditions which process can be carried out on a relatively large scale economically and efficiently.

Summary of The Invention

The present invention relates to the discovery of an aqueous system for the production of metal

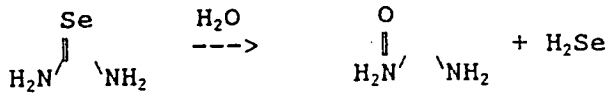
chalcogenide nanocrystalline salts such as zinc selenide, from a hydrolyzable chalcogen carbonyl compound, such as selenourea, by simple hydrolysis thereof under alkaline conditions in the presence of water soluble metal hydroxide, such as zinc hydroxide in the form of the zincate ion, i.e., $Zn(OH)_4^{-2}$.

Selenourea is commercially-available and readily hydrolyzable under aqueous basic conditions in the presence of the zincate ion to form zinc selenide. The zinc selenide is insoluble in the alkaline aqueous vehicle and precipitates over time in the form of nanocrystallites or quantum dots of the zinc selenide.

The essential advantages of the present process, with respect to the production of zinc selenide, are the commercial availability and stability of the reactants, namely the seleno carbonyl compounds, preferably selenourea, and the alkaline-water-soluble form of zinc hydroxide, namely the zincate ion, and their ability to react at low or room temperatures to form the metal chalcogenide salt, namely zinc selenide, which crystallizes out of the aqueous alkaline

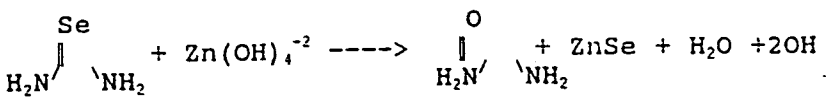
reaction medium in the form of nanocrystallites or quantum dots.

The chalcogen carbonyl reactant, preferably selenourea, contains selenium in the correct oxidation state for the production of quantum dots, and is capable of undergoing hydrolysis under aqueous conditions, as illustrated:



Other selenium compounds such as hydrogen selenide and sodium selenide are not readily commercially available due to their inherent instability in air.

The available, stable seleno carbonyl compounds are easily hydrolyzable in both acidic and alkaline aqueous media but the present aqueous reaction medium must be alkaline in order to solubilize the zincate ion and to precipitate the formed zinc selenide, which is soluble in acidic aqueous media. The balanced equation for the formation of zinc selenide from selenourea and zincate is illustrated:



The following example is given to illustrated preferred procedures for producing zinc selenide quantum dots according to the present invention

The reactants are produced in the following manner, using deionized water through which nitrogen gas has been bubbled for 15 minutes and which is thereafter degassed under vacuum.

A sodium hydroxide solution is prepared by making 100 ml of 0.2 M NaOH in the degassed water, placing a septum thereover, and bubbling nitrogen gas therethrough.

A zinc chloride solution is prepared by making 100 ml of 0.1 M $ZnCl_2$ in the degassed water, placing a septum thereover, and bubbling nitrogen gas therethrough.

A seleno-urea solution is prepared by placing 1 gram of seleno-urea in a flask and adding 84 ml of water and a stir bar. Immediately place a septum on the flask and bubble nitrogen into the

flask, with stirring, until the seleno-urea is in solution. It will form a pale orange solution.

The reaction is carried out by adding 2 ml of the 0.2M NaOH to a 15 ml glass tube containing 6 ml of the water. Then add 1 ml of the 0.1M $ZnCl_2$ solution, at which time a white floc may form. Next a septum is placed on the glass tube and nitrogen is bubbled in, after which 1 ml of the seleno-urea solution is added.

The quantum dots of zinc selenide can be formed in the glass tube by carrying out any of the following procedures:

(a) The glass tube may be stoppered, and placed in a 65°C bath for 10 minutes. A pale orange precipitate will appears which, after centrifuging and decanting of the supernatant, provides an aqueous suspension containing quantum dots of zinc selenide.

(b) The glass tube may be treated as above to form the pale orange precipitate. However, the glass tube is allowed to set for one week before it is centrifuged, the supernatant is decanted and the aqueous suspension is analyzed

for quantum dots of the zinc selenide.

(c) The glass tube may be treated as in procedure (b) above except that it is not placed in a 65°C bath. The stoppered tube remains at room temperature. This procedure is most preferred.

It will be apparent to those skilled in the art, in the light of the present disclosure, that the present aqueous process is also useful for the formation of other metal chalcogenide salts from hydrolyzable chalcogen carbonyl compounds, i.e., carbonyl compounds of sulfur, selenium or tellurium in the presence of the desired metal ions and at the appropriate pH for the dissolution of the reactants and for the precipitation of the formed metal chalcogenide salt.

It should be understood that the foregoing description is only illustrative of the invention. Various alternatives and modifications can be devised by those skilled in the art without departing from the invention. Accordingly, the present invention is intended to embrace all such alternatives, modifications and

variances which fall within the scope of the appended claims.

CLAIMS

What is claimed is:

1. A process for the preparation of metal chalcogenide nanocrystalline salts in an aqueous alkaline reaction medium comprising hydrolyzing a chalcogen carbonyl compound in the presence of a water-soluble metal hydroxide to form and crystallize the metal chalcogenide nanocrystalline salt in the form of quantum dots.

2. The process according to Claim 1 in which the metal chalcogenide salt is zinc selenide.

3. The process according to Claim 1 in which the chalcogen carbonyl compound comprises a seleno carbonyl compound.

4. The process according to Claim 3 in which the seleno carbonyl compound comprises selenourea.

5. The process according to Claim 1 in which the aqueous alkaline reaction medium comprises zinc hydroxide containing zincate ions $Zn(OH)_4^{-2}$.

6. The process according to Claim 1 in which the aqueous alkaline reaction medium comprises sodium hydroxide to which is added zinc chloride to form zinc hydroxide containing zincate ions $Zn(OH)_4^{-2}$.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/22420

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C01B 17/20, 19/00, 19/04; C01G 9/02, 9/08

US CL :423/104, 508, 509, 511, 561.1, 566.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/104, 508, 509, 511, 561.1, 566.1; 252/519.4, 519.51

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,714,339 A (VECHT) 30 January 1973, col. 1 lines 3-7 and col. 4 lines 16-40.	1-4
Y	MURRAY, C. B. et al. "Synthesis and Structural Characterization of II-VI Semiconductor Nanocrystallites (Quantum Dots)" Supplement to Z. Phys. D. 1993, Volume 26 S, pages 231-233, especially page 232 column 1.	1
Y	JP 54-115,698 A (CENTRAL GLASS KK) 08 September 1979, see the English abstract.	5-6
A	LOW, M. P. et al. "The fabrication of light-emitting devices from hot-pressed ZnSe powders" Journal of Materials Science. January 1978, Vol. 13, No. 1, pages 72-76.	1-6

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
18 FEBRUARY 1998	16 MAR 1998

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	TIMOTHY C. VANOY
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/22420

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MURRAY, D. J. et al. "Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites" Journal of the American Chemical Society. 22 September 1993, Vol. 115, No. 19, pages 8706-8715.	1-6
A	GRANT, R. et al. (editors) GRANT & HACKH'S CHEMICAL DICTIONARY. 5th. edition, 1987, McGraw-Hill Book Company U. S. A., ISBN 0-07-024067-1, pages 114-115.	1-6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/22420

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS FILE JPO
L1 ALKALI(W)METAL(W)HYDROXIDE#
L2 ZINC(W)(HALIDE OR CHLORIDE OR IODIDE OR FLUORIDE)
L3 (ZINC OR ZINCATE)(W)HYDROXIDE
L4 L1 AND L2 AND L3
L5 L1 AND L3